Energy transfer from semiconductor nanocrystal monolayers to metal surfaces revealed by time-resolved photoluminescence spectroscopy

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Energy transfer from semiconductor nanocrystal monolayers to metal surfaces revealed by time-resolved photoluminescence spectroscopy

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We studied photoluminescence (PL) and energy transfer dynamics in CdSe nanocrystal (NC) assembled monolayers on Au surfaces. The close-packed CdSe NC monolayers were fabricated using the Langmuir–Blodgett method on spin-coated inert polymer films on rough-surface Au substrates. The PL intensity and PL decay time were dependent on the distance between the CdSe NCs and Au surfaces. These observations indicate that the metal-semiconductor distance and the luminescence-energy dependences of the energy transfer rate can be understood in terms of the Coulomb interaction between excitons in NCs and plasmons on the Au surfaces. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2906369]

The creation of unique materials and devices on a nanoscale level is of great interest from the perspectives of fundamental physics and technological applications. One of the most versatile methods of fabricating such materials is to assemble nanoscale building blocks. Semiconductor nanocrystals (NCs) are one of the most promising types of nanoscale building blocks because of their size-dependent optical and electronic properties and their potential for use in optoelectronic applications such as lasers, light emitting diodes, and solar cells.[1–4] Many studies have focused on explaining the many unique optical phenomena and energy transfer in isolated, coupled, and assembled semiconductor NCs.[5–10] The electronic interaction of semiconductor NCs with metal surfaces has attracted special attention from the viewpoint of plasmonics.[11,12] At the nanoscale metal surfaces, surface plasmons create a strong electromagnetic field, which results in enhanced photoluminescence (PL) from NCs.[13–15] However, the interaction between luminescent materials and metals also increases nonradiative decay rates due to the energy transfer from luminescent materials to metals via electromagnetic interaction,[8,13,15] and this results in PL quenching. Thus, there is still a lot to be learned about the nature and control of the interaction between semiconductor NCs and metals.

Time-resolved PL spectroscopy is one of the most useful methods for understanding the energy transfer between semiconductors and metal surfaces. However, it is difficult to measure the PL dynamics of individual NCs in the picosecond and nanosecond time regions. In addition, the energy transfer and interaction strength between NC excitons and plasmons are sensitive to the surface roughness of metal substrates and the local environment around the NCs.[5,7] To reduce the spatial nonuniformity of samples and to magnify the observed PL intensities, we fabricated a close-packed monolayer of CdSe using the Langmuir–Blodgett (LB) technique. In this letter, we describe the PL dynamics of close-packed CdSe NC monolayers on spin-coated inert polymer films on Au substrates. We controlled the PL decay rate and the PL intensity by varying the thickness of the polymer between the CdSe NCs and the Au film. Our observations are explained in terms of the energy transfer between the semiconductor NCs and the metal surface.

We used CdSe/ZnS core/shell NCs (Evident Technologies) with an average core size of 5 nm. The details of the fabrication and characterization of Au films were reported in our previous paper.[7] The Au films with feature surface height variations of about ±5 nm were fabricated on glass substrates at room temperature using an Ar^+ sputtering method. The surface features of the Au film were confirmed by using an atomic force microscope. The polymethylmethacrylate polymer thin film was spin coated on the Au films, and then the close-packed CdSe NC monolayer, as shown in Fig. 1(a), was formed using the LB technique. These multilayer sample structures are illustrated in Fig. 1(b), where the distance between the Au surface and the CdSe NCs is defined as $\Delta = d + R$, where d is the polymer thickness and R (=5 nm) is the radius of the CdSe/ZnS NCs. The samples with the distance of 5, 11, 17, 20, 26, 35, and 43 nm were used. The average thickness d of the polymer film was determined by ellipsom-

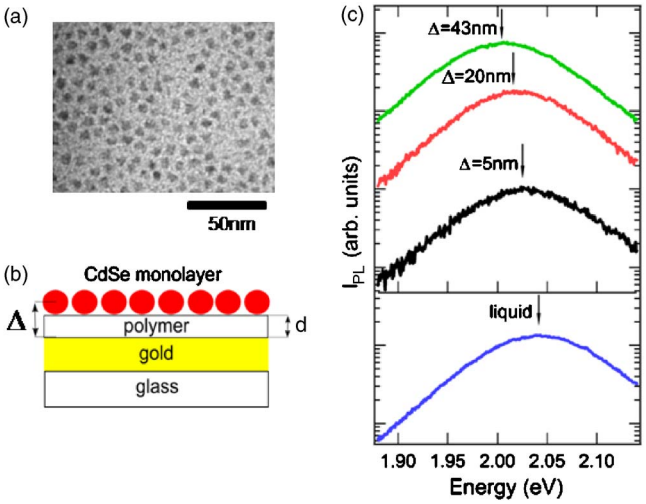

FIG. 1. (Color online) (a) Typical transmission electron microscope image of close-packed CdSe NC monolayer. (b) Schematic illustration of the sample. (c) Time-integrated PL spectrum for samples with distances Δ of 5, 20, and 43 nm (upper) and for CdSe NCs dispersed in chloroform (lower). PL energies are identified by the arrows.

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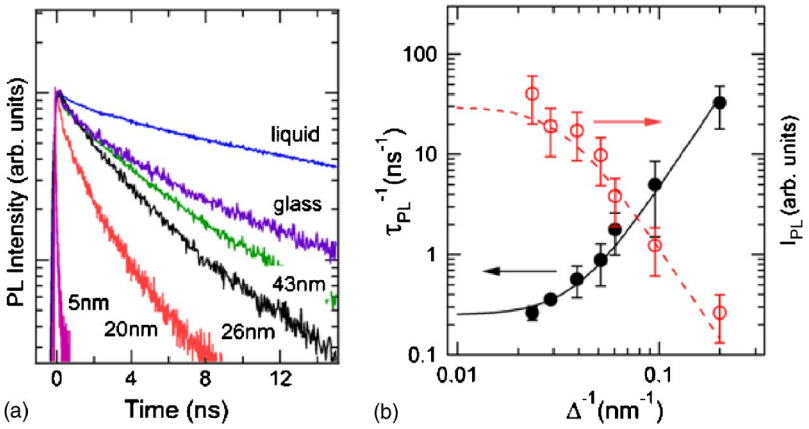

FIG. 2. (Color online) (a) PL decay dynamics for various distances of Δ (5, 20, 26, and 43 nm) between NCs and gold substrates. The PL intensity was spectrally integrated between 2.00 and 2.03 eV. (b) PL lifetime and time-integrated PL intensity as a function of the distance between the CdSe NCs monolayer and the Au film. The solid and dashed curves are fitting ones, $\tau_{PL}^{-1} = a + c\Delta^{-x}$ and $I_{PL} = 1/(a + c\Delta^{-x})$, respectively.

etry of polymers on Si substrate prepared under the same conditions because it is difficult to measure the polymer thickness on rough-surface Au films. We estimated that the typical errors of the thickness are approximately ±5 nm or less and this is caused primary from the roughness of the Au films. Time-resolved PL spectra were measured under 150 fs and 1 kHz pulses at room temperature by a streak camera and a monochromator. The excitation photon energy was tuned to 2.75 eV for the band-to-band excitation to eliminate the plasmon resonance enhancement effect in optical absorption.[7]

Figure 1(c) shows typical time-integrated PL spectra of the CdSe NCs monolayer films for different distances Δ. PL peak energies of these spectra roughly correspond to the PL spectrum of CdSe NCs dispersed in chloroform, as shown in the lower part of Fig. 1(c). However, we note that the PL energy of the close-packed CdSe monolayer shifts to a lower energy level compared to the case of the solution sample and that the PL peak energy slightly depends on the polymer thickness. These spectral changes suggest that energy transfer occurs between CdSe and CdSe NCs, and between CdSe NCs and metal surfaces.

We measured the time-resolved PL spectra to more directly study the energy transfer dynamics. Figure 2(a) shows the decay curves of PL intensities of approximately 2.0 eV in samples with various distances Δ. The PL lifetime in the close-packed monolayer film is shorter than that in chloroform solutions. This reduction suggests that the PL lifetime in the CdSe monolayers on the glass is governed by the nonradiative recombination of excitons in NCs and the energy transfer from small NCs to large NCs, which have lower exciton energies. Furthermore, the PL decay increases with decreased values of Δ, the distance between the Au surface and the CdSe NCs monolayer. This can be attributed to energy transfer from NCs to surface plasmons of the Au surfaces.

Figure 2(b) summarizes the distance dependence of the PL lifetime and the time-integrated PL intensity. Here, the decay time τ_{PL} is defined as the time at an intensity of I_0/e, where I_0 is the PL intensity at zero delay time. There is a close relationship between the PL decay rate and the PL intensity. The reduction of both the PL lifetime and the PL intensity simultaneously occur. PL quenching only occurs in the CdSe NCs monolayer in close proximity to the Au films.

In the NCs-metal complexes, the PL lifetime can be described as

$$\tau_{PL}^{-1} = \tau_{int}^{-1} + \tau_{ET-sem}^{-1} + \tau_{ET-metal}^{-1}, \quad (1)$$

where τ_{int}^{-1} is the exciton decay rate in NCs including radiative and nonradiative recombination, τ_{ET-sem}^{-1} is the energy transfer rate between CdSe NCs, and $\tau_{ET-metal}^{-1}$ is the energy transfer rate from CdSe NCs to surface plasmons of the Au substrates. Since the τ_{int}^{-1} and τ_{ET-sem}^{-1} are independent of the distance Δ, the distance-dependent τ_{PL}^{-1} means that the energy transfer rate from NCs to Au surfaces determines the PL dynamics, $\tau_{ET-metal}^{-1} \gg \tau_{int}^{-1} + \tau_{ET-sem}^{-1}$ and $\tau_{PL}^{-1} \cong \tau_{ET-metal}^{-1}$ in the CdSe NCs monolayer in close proximity to the Au films. Considering the Coulomb interaction between excitons and plasmons, the distance dependence of the energy transfer rate is usually given by $\tau_{ET-metal}^{-1} \propto \Delta^{-x}$, where $x=4$ in the surface energy transfer approximation[16] and $x=6$ in the point dipole approximation.[17] The solid and dashed curves in Fig. 2(b) are the result of fitting, $\tau_{PL}^{-1} = a + c\Delta^{-x}$ and $I_{PL} \propto 1/(a + c\Delta^{-x})$, where $a = 0.25$ ns^{-1} is the PL decay rate on the glass substrate and c is fitting parameter. In this case, the obtained value, $x \simeq 3.1$, is closer to $x=4$ than $x=6$. Consequently, the distance dependent PL dynamics shows that the PL dynamics is determined by energy transfer between excitons and surface plasmons.

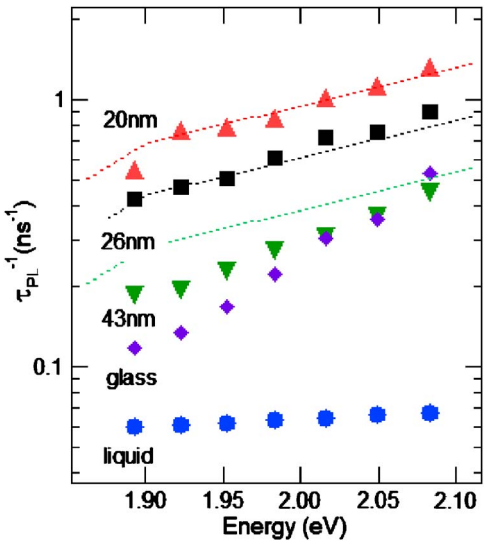

FIG. 3. (Color online) PL lifetime in the CdSe/Au sample with distances of 20 nm (solid triangle), 26 nm (solid square), and 43 nm (open square) as a function of PL energy, and in the CdSe NCs on glass substrate and in chloroform solution.

Figure 3 shows the PL decay rate (τ_{PL}^{-1}) for various samples as a function of the PL energy. For all monitored photon energies, the PL lifetimes of NCs decrease with a decrease in Δ, the distance between NCs and Au surfaces. In addition, the energy dependence of the PL decay rate depends on the distance Δ; thin films exhibit small PL energy dependence. This indicates that the energy transfer from CdSe NCs to the Au film becomes the primary channel, more than that between CdSe NCs in the samples with small values of Δ. In the Δ=43 nm film, however, the PL decay rate and its energy dependence are similar to those on the glass substrate. These results show that in the large Δ samples the energy transfer channel from excitons to plasmons is negligibly small and the PL dynamics is determined by the energy transfer between CdSe NCs. The energy dependence of the PL decay rate in the small Δ samples reflects that of the energy transfer rate from NCs to surface plasmons.

Finally, we comment on the energy dependence of the energy transfer rate from NCs to Au surfaces shown in Fig. 3. Here, we use a dipole approximation assuming that the rough Au films are large Au NCs, and both CdSe and Au NCs are a point dipole. In this simple model, the energy transfer time is analytically given by[17]

$$\tau_{ET-metal}^{-1}(\omega_{PL}) \propto \mu_{exc}^2 \, \mathrm{Im}\left[\frac{\varepsilon_{metal}(\omega_{PL}) - \varepsilon_b}{\varepsilon_{metal}(\omega_{PL}) + 2\varepsilon_b}\right], \quad (2)$$

where ω_{PL} is the PL frequency, μ_{exc} is the dipole moment of an exciton in the NCs, ε_{metal} is the dielectric constant of Au NCs, and ε_b is the background dielectric constant. Calculation results using Eq. (2) are shown in Fig. 3, where ε_b is 2.2 (the dielectric constant of the polymer) and μ_{exc}^2 is assumed to be constant. We attempted to reproduce the experimental data on the 20 nm films in Fig. 3 by adjusting the value of μ_{exc}^2. The best-fit results for the 20 nm films are indicated with a dotted curve. The energy dependence of the dielectric constant ε_{metal} determines that of the energy transfer rate in the thin polymer samples. For all the samples with various distances Δ, the energy dependence of the PL decay rate was reproduced well as a function of both the energy dependence and the Δ dependence ($\tau_{ET-metal}^{-1} \propto \Delta^{-x}$) of the energy transfer rate, as shown by dotted lines. In the thick polymer sample, the discrepancy between the experimental results and the fitted curve is due to the contribution of the energy transfer between CdSe NCs. It is clear that the energy transfer to the surface plasmons can be temporally and spectrally tuned by controlling the interaction between the semiconductor NCs and metal films.

We have examined the PL dynamics and energy transfer in CdSe NC monolayers on Au surfaces as a function of the distance between the CdSe NCs and the Au surfaces. The PL decay rate increases and the PL intensity decreases with a decrease of the CdSe–Au distance. Rapid energy transfer occurs from excitons in NCs to plasmons on rough metal surfaces. The energy transfer mechanism is understood as an electromagnetic interaction between CdSe NCs and Au substrates.

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